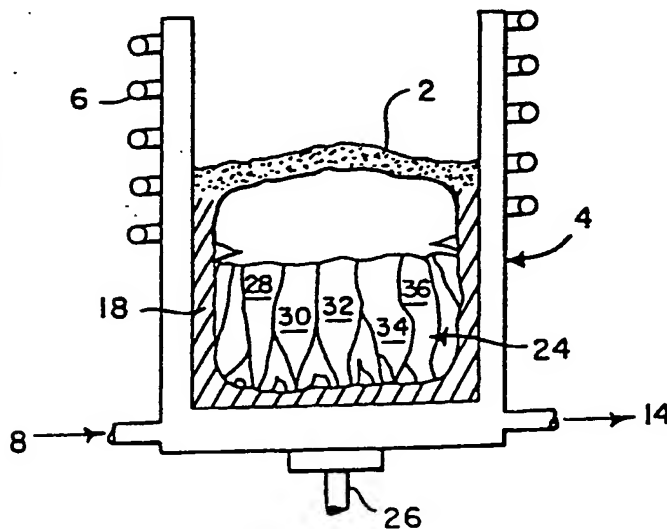




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(54) Title: SINGLE-CRYSTAL PARTIALLY STABILIZED ZIRCONIA AND HAFNIA CERAMIC MATERIALS		
(57) Abstract A method of making a single crystal of partially stabilized zirconium dioxide or hafnium dioxide by: mixing powdered zirconium dioxide or hafnium dioxide with 2 to 7 mole percent of a stabilizing agent, such as, an oxide of either a transition metal or a rare earth element; heating the above mixture until it melts; and cooling the mixture by withdrawing it from the heating zone at a rate of 2-30mm. per hour. The resulting crystals comprise a matrix of cubic crystalline materials and numerous minute tetragonal and possibly monoclinic crystalline materials. Such crystals can be created having a flexure strength of approximately 200,000 psi and a fracture toughness of approximately 7,85 Ksc.		



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SINGLE-CRYSTAL PARTIALLY STABILIZED
ZIRCONIA AND HAFNIA CERAMIC MATERIALS

Description

Technical Field

- 5 This invention is in the field of ceramics, crystallography and chemistry.

Background

- 10 Zirconium (Zr) is an element with an atomic number of 40, an atomic weight of 91.22, and a valence of 4. Hafnium (Hf) has an atomic number of 72, an atomic weight of 178.49, and a valence of 4. The predominant oxidized forms are commonly referred to as zirconia (ZrO_2) and hafnia (HfO_2).

- 15 Zirconia and hafnia each have three principle crystal structures: cubic, tetragonal, and monoclinic. As zirconia is cooled after being heated to its molten state in the absence of stabilizing agents, it progresses through all three crystal structures. In the absence of stabilizing agents, the cubic
20 structure is the most stable, and the monoclinic structure is the least stable. At low temperatures, these relative stabilities are reversed. Therefore, during cooling, zirconia normally progresses from the cubic structure, to the tetragonal structure,
25 to the monoclinic structure.

- 30 Cubic zirconia can be stabilized by the addition of sufficient quantities of one or more stabilizing agents. For example, U. S. patent 4,153,469 (Alexandrov et al., 1979) discloses that 10 to 30 mole percent of yttrium oxide (Y_2O_3 , commonly called yttria) stabilizes zirconia in the cubic crystal configuration. Such crystals are transparent and have a high optical quality, and are used as



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artificial precious stones in jewelry, and as laser elements. Oxides of other elements may be added to obtain colored zirconia crystals.

Partially stabilized zirconia (PSZ) does not
5 have the desirable transparent optical properties that fully stabilized cubic zirconia possesses. However, PSZ possesses certain other properties that are of interest in the ceramic field.

"Partially stabilized" is a functional term.
10 If less than an ascertainable amount of stabilizing agent is added to molten zirconia, then not all of the zirconia will retain the cubic crystal configuration when it is cooled to room temperature. If this is the case, several things can happen. It is
15 possible for localized areas of cubic, tetragonal and monoclinic crystals to be interspersed in a PSZ crystal. One possible way this can occur is for tetragonal particles to exist in a matrix of cubic zirconia. See D. L. Porter et al., "Mechan-
20 isms of Toughening Partially Stabilized Zirconia (PSZ)", J. Am. Ceram. Soc., 60, No.3-4, pp 183-184 (1977).

Ceramics are nonmetallic, inorganic,
materials that are most commonly used for structural
25 purposes. The structural properties of ceramics, especially at high temperatures, are of great importance. Two common indices of these properties are:

1. Tensile strength, which measures how
30 much force must be applied to pull apart a ceramic piece with a known cross-sectional area. This parameter can be expressed in



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terms of pounds per square inch (psi) or pascals (Pa). A pascal is equal to 1 newton of force applied to 1 square meter; a megapascal (MPa) is equal to 1 million pascals. One MPa is equal to approximately 145 psi.

Tensile strength is often approximated by measuring flexure strength. Instead of pulling a specimen apart along one axis (which would determine tensile strength), a specimen is bent until it breaks, and the maximum tensile force (which occurs along one edge of the specimen) is calculated. Flexure strength is measured in psi or MPa. It tends to be somewhat higher than tensile strength, since a flaw in the interior of a specimen that might cause a tensile break might not cause a flexure break.

2. Fracture toughness, usually expressed as K_{1C} . Fracture toughness is usually measured by creating a flaw of a known size in the specimen being studied, then breaking the specimen under controlled loading conditions using, for example, a double cantilever beam (DCB) technique. The force required to break the specimen is then divided by the cross-sectional area of the break times the square root of the length of the flaw. K_{1C} is therefore expressed in terms of newtons per meter $^{3/2}$, or in pascals times meter $^{1/2}$.



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Porter et al., cited above, recognized that heat-treated PSZ had a higher degree of fracture toughness than fully stabilized cubic zirconia. The maximum toughness they observed in PSZ was K_{IC} of approximately $6 \text{ MN/m}^{3/2}$, compared to the toughness of cubic zirconia of $2.8 \text{ MN/m}^{3/2}$. Those researchers were studying the toughness of polycrystalline PSZ that was formed by conventional pressing and sintering techniques. In this form, tetragonal crystallite inclusions formed by precipitation (herein referred to as crystallites; sometimes referred to as precipitates) are believed to exist along two or more major axes within a crystal grain of cubic zirconia. The alignment of the tetragonal crystallites and the cubic matrix in adjacent but distinct grains often is skewed, creating a boundary or a face between the grains. These faces between the grains tend to have substantially less tensile strength than the cross section of a grain. Therefore, when subjected to stress, grain boundaries in polycrystalline PSZ can be sources of fractures, thereby limiting the strength and toughness of PSZ.

In addition, grain boundaries in polycrystalline PSZ impede (1) the ionic conductivity of zirconia, thereby limiting a number of valuable uses of zirconia, such as detectors for analyzing the contents of gases, and (2) the electromagnetic transmissibility of zirconia, thereby limiting the use of zirconia in optical and radio applications that require high strength and toughness.

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Disclosure of the Invention

The Applicants have discovered that single crystals of partially stabilized zirconia (PSZ) possess surprisingly superior ceramic properties.

- 5 These large single crystals are believed to comprise a dispersion of numerous tetragonal or monoclinic crystallites within a matrix of cubic crystalline material. These single crystals possess tensile strength and fracture toughness characteristics
- 10 that greatly exceed the tensile strength and fracture toughness of any practical ceramic material ever discovered prior to this invention.

- The experimental results obtained thus far by the Applicants indicate that large single crystals
- 15 can also be formed of partially stabilized hafnium dioxide, and that such crystals exhibit superior ceramic properties when compared to polycrystalline partially stabilized hafnium dioxide, or to fully stabilized cubic hafnium dioxide.

- 20 The results obtained to date by the Applicants also indicate that large single crystals of PSZ or PSH can be partially stabilized by the oxides of numerous transition and rare earth elements, including yttrium, calcium, magnesium, scandium, samarium,
- 25 gadolinium, dysprosium, ytterbium, lutecium, cerium, praseodymium, neodymium, europium, holmium, erbium, thulium, or turbium.

- The Applicants have invented a method of creating such single crystals that are large enough
- 30 for ceramic uses. Zirconia and hafnia are partially stabilized by adding a predetermined quantity of



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stabilizing agent to a predetermined quantity of zirconia or hafnia. This normally is accomplished by mixing the stabilizing agent with the zirconia or hafnia while both substances comprise fine powders at room temperature. The mixture is then heated to a melting temperature (normally in excess of 2500°C). This can be accomplished by inductive high-frequency radio waves. The powder is placed in a water-cooled vessel prior to heating. The cooling surfaces of the vessel prevent the powder that touches the cooling surfaces from becoming molten. This forms a shell (often called a skull) of sintered material between the cooling surfaces and the molten zirconia or hafnia; this avoids problems that can arise when extremely hot molten substances come in contact with solid surfaces.

After heating the zirconia or hafnia mixture at the proper temperature for an appropriate period of time, the molten mixture is allowed to cool slowly, to promote the formation of a regular crystalline structure. This can be accomplished by slowly lowering the vessel out of the heating field, and reducing or eliminating the radio frequency power at an appropriate time. The resulting material comprises a large (from approximately 3 inches to over 1 foot in diameter) block of crystalline material surrounded by a sintered shell. The shell is removed by mechanical means. The resultant crystalline body typically comprises several relatively small (largest dimension approximately 1/4 inch to 1 inch) crystals near the bottom of the block of material, interspersed with larger crystals that may exceed 1 inch in diameter and several inches in length. Although these crystals



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do not adhere tightly to each other, each crystal has a single consistent composition of tetragonal and possibly monoclinic crystallites within a matrix of cubic crystalline structure. Each such crystal
5 can be referred to as a single grain.

These crystals may be machined into desirable configurations using diamond-edged cutting instruments and other conventional techniques. In addition, numerous crystals may be plastic-deformed into
10 desirable configurations by press-forging at elevated temperatures, although problems involving oxygen loss may require special techniques.

Single-crystal PSZ has ionic conductivity and electromagnetic transmissibility properties that are
15 superior to polycrystalline PSZ. These properties allow for improvements in the use of PSZ for purposes that involve ionic conductivity or electromagnetic transmissibility.



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Description of Figures

Figure 1 is a cross section of an apparatus used to heat zirconia or hafnia mixed with a stabilizing agent to the molten state.

5 Figure 2 is a cross section of zirconia or hafnia mixture being withdrawn from the heating zone.

10 Figure 3 is a cross section of zirconia or hafnia mixture after it has cooled into a crystalline structure.

Figure 4 is a graph that indicates the flexure strength and fracture toughness of several partially stabilized zirconia crystals.

15 Figure 5 is a graph that indicates the flexure strength of various ceramic materials as a function of temperature.



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Best Mode of Carrying Out the Invention

In one preferred embodiment of this invention, 450 grams of Y_2O_3 (yttria) powder were dry-mixed with 8,550 grams of ZrO_2 (zirconia) powder, to give
5 a mixture containing 5% yttria by weight. The powders were mixed by placing both in a polyethylene jar, and roll-milling for several hours. Alternatively, V-blending or other conventional mixing means may be used. The mixture was then loaded into a
10 6 inch diameter skull-melting furnace, which has a standard melt capacity of 9 kilograms of zirconia. The powder rests upon a water-cooled plate, and is surrounded by vertical copper tubes which contain circulating cooled water. There is no lid on this
15 furnace, so the top of the powder is exposed to the air. The loaded furnace was then placed in the middle of a radio frequency generating coil, operating at up to 50 kilowatts of output at 2.5 to 3.5 megahertz.

The skull container is first charged with 3,000
20 grams of mixed powder, and a 30 gram cluster of zirconium metal. Since the mixed powder at room temperature does not absorb the energy of the high-frequency radio waves, the zirconium metal is added to begin the heating process. The metal chips heat rapidly
25 and cause the surrounding powder to be heated to a temperature at which they begin to absorb the high-frequency waves directly. After approximately 10 minutes, the interior of the 3030 gram initial charge is molten. It is contained within a sintered shell
30 of unmelted powder, which is being cooled by the water in the copper tubes. This sintered shell (often called a skull) prevents the molten zirconia from coming into direct contact with the copper tubes.

The remaining 6 kilograms of powder mixture are
35 added to the skull container over a period of approximately one hour. As additional feed material



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is added, the radio frequency input power is slowly increased to approximately 35 kilowatts. The molten charge is allowed to remain stationary for a period, while convection currents mix the zirconia and yttria thoroughly. The skull container is then mechanically lowered at a fixed rate of about 1.1 centimeter per hour. This allows for the bottom portion of the skull container to leave the heating zone and begin the cooling process, allowing crystals to begin forming near the bottom of the skull. Simultaneously with the lowering motion, the skull is rotated with a bi-direction oscillatory motion through an angle of about 45 degrees at a frequency of about 10 times per minute.

After the skull container has been lowered approximately 7.7 centimeters (which takes about seven hours), the radio frequency power is shut off, and the crystals are allowed to cool to room temperature before removal. The cooled crystals are subsequently removed from the skull container. The sintered shell surrounding the crystals is removed, and the crystal grains are separated carefully. Several grains were subsequently analyzed to determine their flexure strength, fracture toughness, and other properties, as described in Example 5-7.

This process is further described by reference to Figures 1 through 3.

As shown in Figure 1, powder mixture 2 is placed in skull container 4. The loaded skull container is then placed within circular high frequency induction heating coil 6. Cooling water enters water inlet 8, and circulates within vertical tubes 10 and container base 12, before exiting through water outlet 14. When heated to the melting point, the interior 16



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of the powder mixture becomes molten. This molten region is surrounded by sintered shell 18, which is prevented from melting because it is in contact with water-cooled tubes 10 and base 12. An unmelted porous crust 20 typically forms above the surface of the melt.

Figure 1 indicates the positioning of the skull container 4 and the mixed powder charge 2 within the region that is heated by induction coils 6. In this position, all of the powder will become molten except for sintered shell 18 and crust 20. Figure 2 indicates that the skull container 4 is being slowly lowered by mechanical means. The bottom of molten region 16 leaves the heated region and begins to form crystals 24 upon the base of the centered skull 18. These crystals initially comprise the cubic crystalline structure, which is the most stable crystalline form at temperatures near the melting point. However, as these crystals cool further, a dispersion of numerous minute crystallites, in the form of tetragonal and possibly monoclinic crystallites, forms within the matrix of the partially stabilized cubic zirconia.

Figure 3 indicates that skull container 4 has been mechanically lowered by mechanical means 26 until crystals 24 have left the region heated by induction coils 6. The crystal region 24 is comprised of numerous individual grains, including grains 28, 30, 32, 34, and 36. Within each of these grains, the tetragonal crystallites are arranged on a regular



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basis. Each of these grains exhibits extremely high flexure strength and fracture toughness. However, the boundary or interface between any two grains is relatively weak, and each grain may be separated
5 easily from the other grains.

Table 1 and Figures 4 and 5 contain data comparing the flexure strength and fracture toughness of the single-crystal PSZ with several other ceramic materials. PSZ 1027 is a commercially available
10 form of zirconia, partially stabilized with about 3.5 weight percent MgO, with a relatively large grain structure. Zyttrite is a form of zirconia, fully stabilized with from 12 to 20 weight percent of yttria, with an intermediate grain size, that is
15 used as a reference standard. Both are polycrystalline substances, formed by conventional pressing and sintering techniques.



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TABLE 1

Comparison of Single-Crystal PSZ with
Other Ceramic Materials
(Average values and ranges)

5	<u>Material</u>	<u>Flexural strength (MPa)</u>	<u>Flexural strength (Kpsi)</u>	<u>Fracture toughness (K_{1c})</u>
	<u>Room temperatures</u>			
10	Single-crystal PSZ	1050-2100	150-300	4-8
	Fully stabilized Cubic Zirconia			
	Single crystal	300-350	40-50	2-2.8
	Polycrystalline	200	30	~ 2
15	Polycrystalline PSZ			
	PSZ 1027 (large grain)	350-630	50-90	4-8
	Zyttrite (inter- mediate grain)	700-1050	100-150	5-8
20	Single crystal Al ₂ O ₃ (sapphire)	350-550	50-80	2
	Polycrystalline Al ₂ O ₃	350-700	50-100	4
	Polycrystalline hot-pressed Si ₃ N ₄	840	120	4-7
25	<u>Elevated Temperatures</u>			
	Single-crystal PSZ at 1500°C	630-770	90-110	4-8
	Cubic zirconium at 1500°C	210-350	30-50	< 2
30	Si ₃ N ₄			
	at 1100°C	490-630	70-90	4-7
	at 1500°C	70-140	10-20	

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EXAMPLESExample 1: Preparation of Powder Mixture

Zirconia (ZrO_2) powder was obtained from Magnesium Elektron, with a purity of 99%. It has an average particle size of approximately 10-16 microns, and contained approximately 2% HfO_2 . Yttria (Y_2O_3) powder was obtained from Megon (purity 99.99%). It had an average particle size of approximately 10-16 microns. Carefully weighed quantities of each powder were mixed by placing both in a polyethylene jar, and rolling the jar on mixing rollers for approximately 12 hours. Approximately 3,000 grams of the mixed powder was placed in a skull container. The skull container comprised a 6 inch diameter water-cooled copper base plate, surrounded by vertical copper tubes at the perimeter of the base plate. Each copper tube contained an inner tube. Cooling water was circulated up through the annulus of each tube, and down through the interior tube.

The loaded skull container was then placed within a circular induction heating coil. The heating coil was powered by a 50 kilowatt radio frequency generator, which operated at 2.5 to 3.5 megahertz.

Example 2: Heating the Zirconia Mixture

A skull container, loaded with a charge of zirconia powder mixed with yttria powder, was placed within a heating coil, as described in Example 1. When the generator power is turned on, the radio waves which are concentrated within the coil excite the zirconia and yttria molecules causing them to become heated. However, since the resistance of zirconia powder at room temperature is too high to



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allow coupling at the frequency used, about 30 grams of zirconium metal (Ventron sponge, purity 99.5%) was placed in a cluster on the surface of the powder. The metal chips heat rapidly and cause the surrounding powder to be preheated to a temperature high enough for direct induction heating. An expanding zone of powder becomes molten, until the entire powder charge becomes molten except for a sintered skull surrounding the molten region. This skull is prevented from becoming molten by being in contact with the cooled base and vertical tubes. In addition, a porous crust may form on the top surface of the molten material, cooled by exposure to the air. A pocket of air may be formed beneath this porous crust.

The remainder of the mixed powder is then added to the skull container in small increments over a period of approximately one hour. As the amount of material in the skull container increases, the heating input power is also increased. When the 9 kilogram charge is contained in the skull, the applied heating power is approximately 35 kilowatts.

After all of the powder is added to the melt, the heating continues for a period of approximately 10 to 20 minutes to allow the molten substance to become thoroughly mixed by convection currents.

Example 3: Controlled Cooling and Crystal Formation

After the molten mixture described in Example 2 is allowed to stand for an appropriate time, the skull container is mechanically lowered at a fixed rate of 1.1 centimeter per hour. Since the induction heating occurs only within a certain region, this removes the bottom of the skull out of the heated area, allowing the molten mixture on the bottom to



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begin cooling and crystallizing. Simultaneously with the withdrawal motion, the skull is also rotated about its axis with a bi-directional oscillatory motion through an angle of 45° at a frequency of 10 times per minute.

During the initial stage of crystal formation, it is believed that the partially stabilized zirconia adopts a cubic crystalline configuration, which is the most stable crystalline configuration at temperatures near the melting point. However, as the crystals are allowed to cool further, it is believed that numerous crystallites, comprising tetragonal and possibly monoclinic crystallites, form within the matrix of cubic zirconia.

During the lowering and cooling operation, the heating power input level, frequency and coupling efficiency are constantly monitored. When the skull container is lowered until the molten/crystalline region is no longer in the region of heating, the heating input power is shut off and the charge is allowed to cool to room temperature before removal.

Example 4: Removal and Grain Separation

The crystals that were formed as described in Example 3 were allowed to cool to room temperature. The entire charge was then removed from the skull container by raising the base plate in relation to the vertical cooling tubes. The sintered shell was removed from the crystals. The remaining crystalline material was in a configuration indicated by grains 28 through 36 in Figure 3. Each grain comprised a matrix of cubic zirconia interspersed with



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minute tetragonal and possibly monoclinic crystallites that were in a consistent pattern throughout that grain.

Example 5: Crystallographic Analysis

5 Crystals with 12 to 20 per cent by weight of yttria were clear or transparent. This indicated that such crystals were fully stabilized in the cubic crystalline configuration. Crystals with 8% by weight of yttria were cloudy, and crystals with 4% by weight
10 yttria were opaque white. This indicated that the number of minute tetragonal and possibly monoclinic crystallites increases with decreasing yttria content. Examination under light microscope, and x-ray diffraction analysis confirmed this correlation. Laue back
15 reflection analysis typically showed a [110] orientation along the length of the columnar crystals for all crystal compositions. Crystals with less than 8% by weight yttria contains an additional and distinct stereographic projection with a [100] orientation,
20 indicating a greater percentage of tetragonal crystallites with a regular orientation within the cubic matrix.

Example 6: Determination of Fracture Toughness

Fracture toughness, commonly expressed as K_{1c} ,
25 was determined by two techniques: indentation using a pyramidal diamond (described by A. G. Evans et al, "Fracture Toughness Determinations by Indentation," J. Amer. Ceramics Soc. 59, Nos. 7-8, pp 371-372 (1976)); and double cantilevered beam analysis
30 (S. W. Freiman et al, "Crack Propagation Studies in Brittle Materials," J. Mat. Sci. 8, No. 11, pp. 1527-1533 (1973). Typical specimen dimensions for the DCB analysis were 1x5x12 mm with a center groove 0.3



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mm wide and 0.6 μ m deep, down the center of one side of the specimen. Both of these tests indicated that K_{Ic} increased from about 1.7 MN/m^{3/2} for cubic zirconia with 20% by weight yttria, to 7.85 MN/m^{3/2} at 4% by weight yttria. Additional data are contained in Table 1 and Figures 4 and 5.

Example 7: Determination of Tensile Strength

3-point flexure tests (0.9 centimeter span; 1 mm/min crosshead speed) were conducted on bars that were 0.22 by 0.23 cm in crosssection, cut parallel with the crystal length and ground lengthwise. The tensile strength of the cubic zirconia was approximately 210 MPa for the 20 and 12 per cent by weight yttria crystals. The tensile strength of 8% by weight crystals increased to approximately 520 MPa, and the tensile strength of 6 and 4 percent by weight yttria crystals increased to approximately 1,000 MPa. The coefficients of variation for all measurements were about 10%. Additional data are contained in Table 1 and Figures 4 and 5.



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Industrial Applicability

The invention described herein has industrial applicability in the manufacture and use of ceramic materials with superior tensile strength and fracture
5 toughness.

Equivalents

Those skilled in the art will recognize or be able to determine using no more than routine experimentation, many equivalents to the specific pro-
10 cedures described herein. Such equivalents are considered to be within the scope of this invention and are intended to be covered by the following claims.



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Claims

1. A ceramic material comprising zirconium dioxide or hafnium dioxide, partially stabilized by a sufficient quantity of stabilizing agent to
5 cause said ceramic material to crystallize in single crystals comprising a dispersion of numerous tetragonal or monoclinic crystallites within a matrix of cubic crystalline material, whereby said crystallites significantly enhance
10 the flexure strength and fracture toughness of said ceramic material.
2. A ceramic material comprising zirconium dioxide or hafnium dioxide, partially stabilized by a sufficient quantity of stabilizing agent to en-
15 hance the flexure strength and fracture toughness of said ceramic material.
3. A ceramic material comprising zirconium dioxide or hafnium dioxide, partially stabilized by a stabilizing agent, said ceramic material com-
20 prising single crystals that have fracture toughness in excess of $4 \text{ MPa/m}^{\frac{1}{2}}$.
4. A ceramic material comprising zirconium dioxide or hafnium dioxide, partially stabilized by a stabilizing agent, said ceramic material com-
25 prising single crystals that have flexure strength in excess of 1000 MPa.
5. A ceramic material comprising a single crystal made of zirconium dioxide or hafnium dioxide, partially stabilized by a stabilizing agent.



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6. A single-crystal ceramic material comprising
from about 93 to about 98 mole percent of
zirconium dioxide or hafnium dioxide, partially
stabilized by about 2 to about 7 mole percent of
a stabilizing agent.
7. A single-crystal ceramic material comprising
from about 93 to about 98 mole percent of
zirconium dioxide or hafnium dioxide, partially
stabilized by about 2 to about 7 mole percent
of a stabilizing agent, whereby said stabilizing
agent significantly enhances the flexure strength
and fracture toughness of said ceramic material.
8. A composition of Claims 1, 2, 3, 4, 5, 6 or 7
wherein said stabilizing agent is an oxide of
an element selected from the following group:
yttrium, calcium, scandium, samarium, gadolinium,
dysprosium, ytterbium, lutecium, cerium,
praseodymium, neodymium, europium, holmium,
erbium, thulium, terbium, magnesium, or titanium.
9. A composition of Claims 1, 2, 3, 4, 5, 6 or 7
wherein said stabilizing agent comprises an oxide
of a transition metal or an oxide of a rare
earth element.
10. A composition of Claims 1, 2, 3, 4, or 5
wherein said ceramic material is comprised of
about 93 to about 98 mole percent of zirconium
dioxide or hafnium dioxide and about 2 to about
7 mole percent of a stabilizing agent.



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11. A method of creating a ceramic material comprising a single-crystal of partially stabilized zirconium dioxide or hafnium dioxide with enhanced tensile and flexure strength and fracture toughness, comprising the following steps:
- 5 (a) Thoroughly mixing powdered zirconium dioxide or hafnium dioxide with a sufficient quantity of powdered stabilizing agent to comprise about 2 to about 7 mole percent of stabilizing agent;
- 10 (b) heating said mixture to a temperature sufficient to melt said mixture;
- 15 (c) cooling said molten mixture by withdrawing said mixture from the heating zone at a rate of from 2 to 30 mm per hour.
12. A method of Claim 11 wherein said stabilizing agent is an oxide of an element selected from the following group: yttrium, calcium, scandium, samarium, gadolinium, dysprosium, ytterbium, lutecium, cerium, praseodymium, neodymium, europium, holmium, erbium, thulium, terbium, magnesium, or titanium.
- 20 13. An improvement of Claim 11 wherein said stabilizing agent comprises an oxide of a transition metal or an oxide of a rare earth element.
- 25 14. A ceramic material created by the method of Claim 11.



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15. An improvement of Claim 11 wherein said ceramic material is machined to convert it into a desired shape.
- 5 16. An improvement of Claim 11 wherein one or more crystals of said ceramic material are press-forged at elevated temperatures to convert said crystals into a desired shape.
- 10 17. A composition of matter comprising zirconium dioxide or hafnium dioxide, partially stabilized by a sufficient quantity of stabilizing agent to cause said zirconium dioxide or hafnium dioxide to crystallize in single crystal, whereby the absence of numerous crystal boundaries in said crystal substantially enhances the ionic conductivity of said crystal in comparison with polycrystalline partially stabilized zirconium dioxide or hafnium dioxide.
- 15 18. In the use of zirconium dioxide or hafnium dioxide for uses involving the property of ionic conductivity, the improvement of using single crystals of partially stabilized zirconium dioxide or hafnium dioxide.
- 20 19. A composition of matter comprising zirconium dioxide or hafnium dioxide, partially stabilized by a sufficient quantity of stabilizing agent to cause said zirconium dioxide or hafnium dioxide to crystallize in single crystal, whereby
- 25



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the absence of numerous crystal boundaries in said crystal substantially enhances the electromagnetic transmissibility of said crystal in comparison with polycrystalline partially stabilized zirconium dioxide or hafnium dioxide.

20. In the use of zirconium dioxide or hafnium dioxide for uses involving the property of electromagnetic transmissibility, the improvement of using single crystals of partially stabilized zirconium dioxide or hafnium dioxide.

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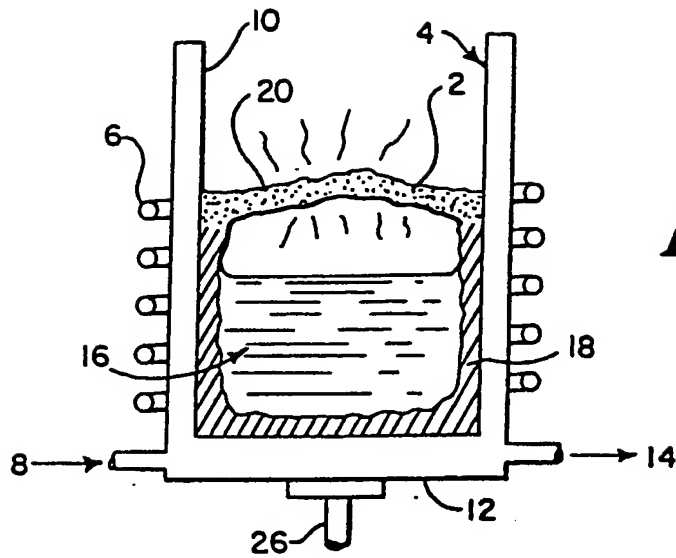


Fig. 1

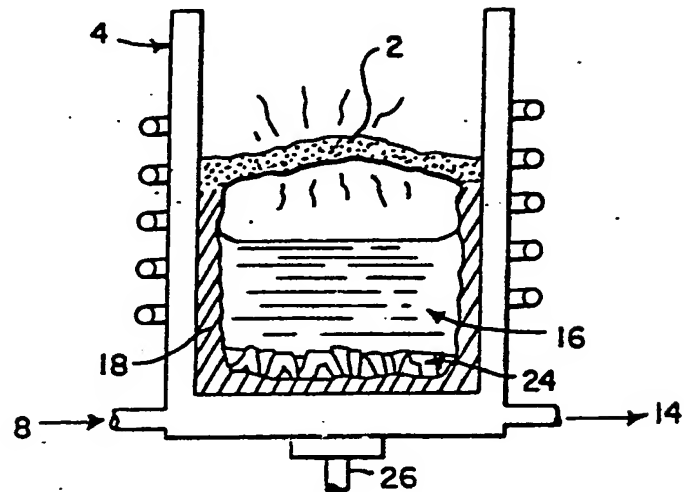


Fig. 2

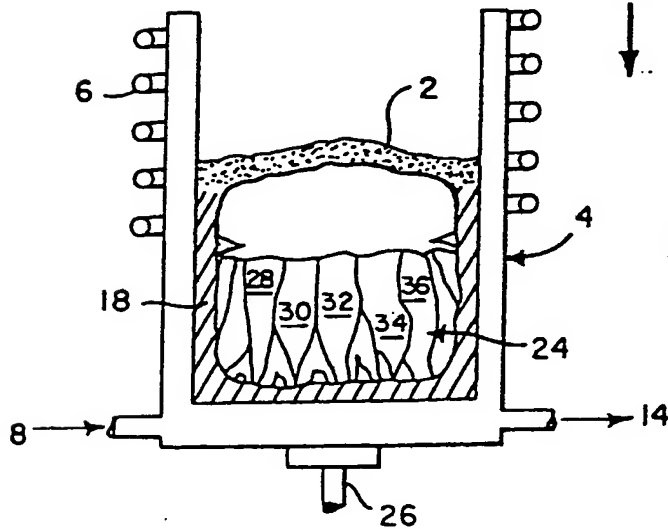
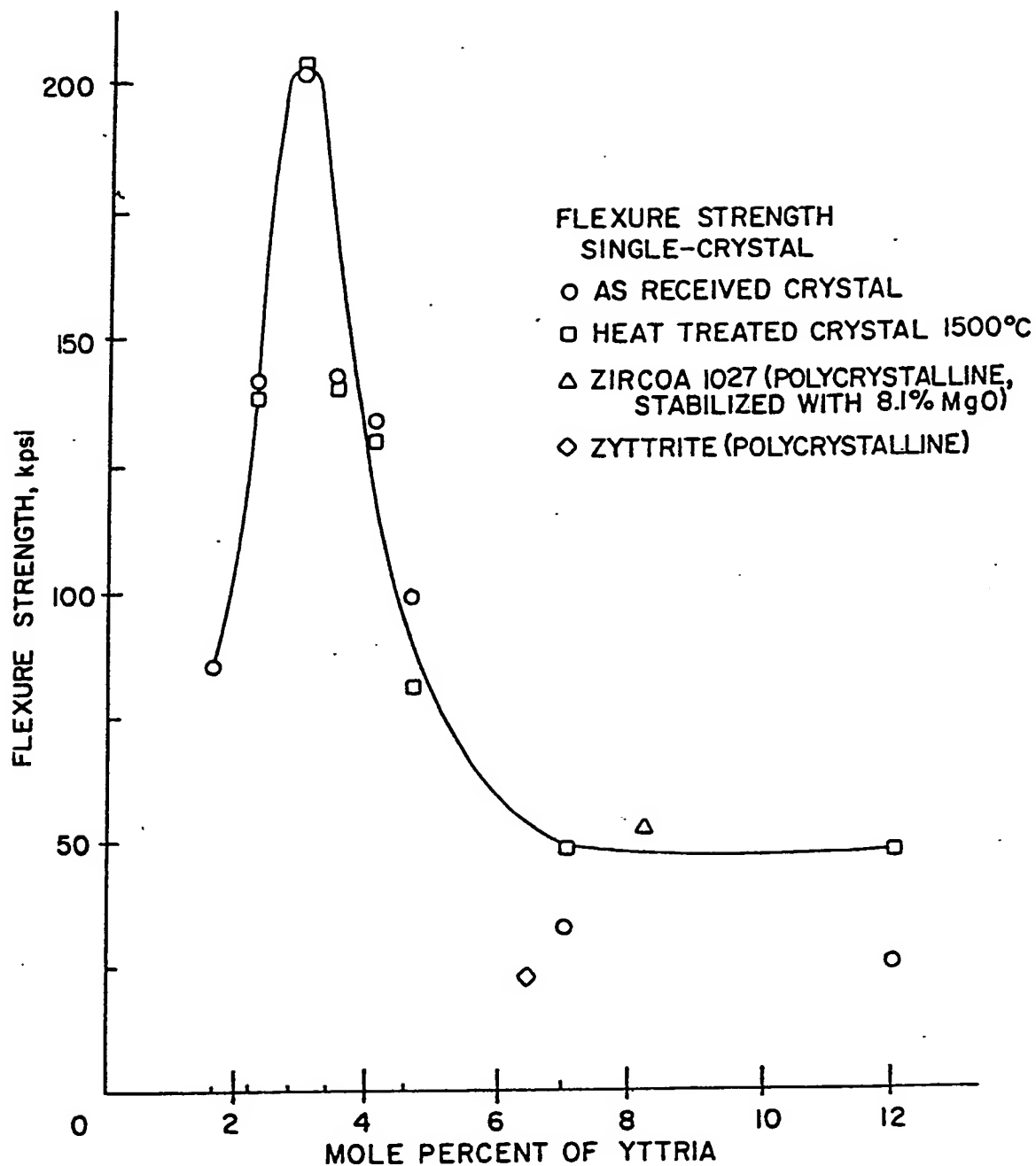


Fig. 3

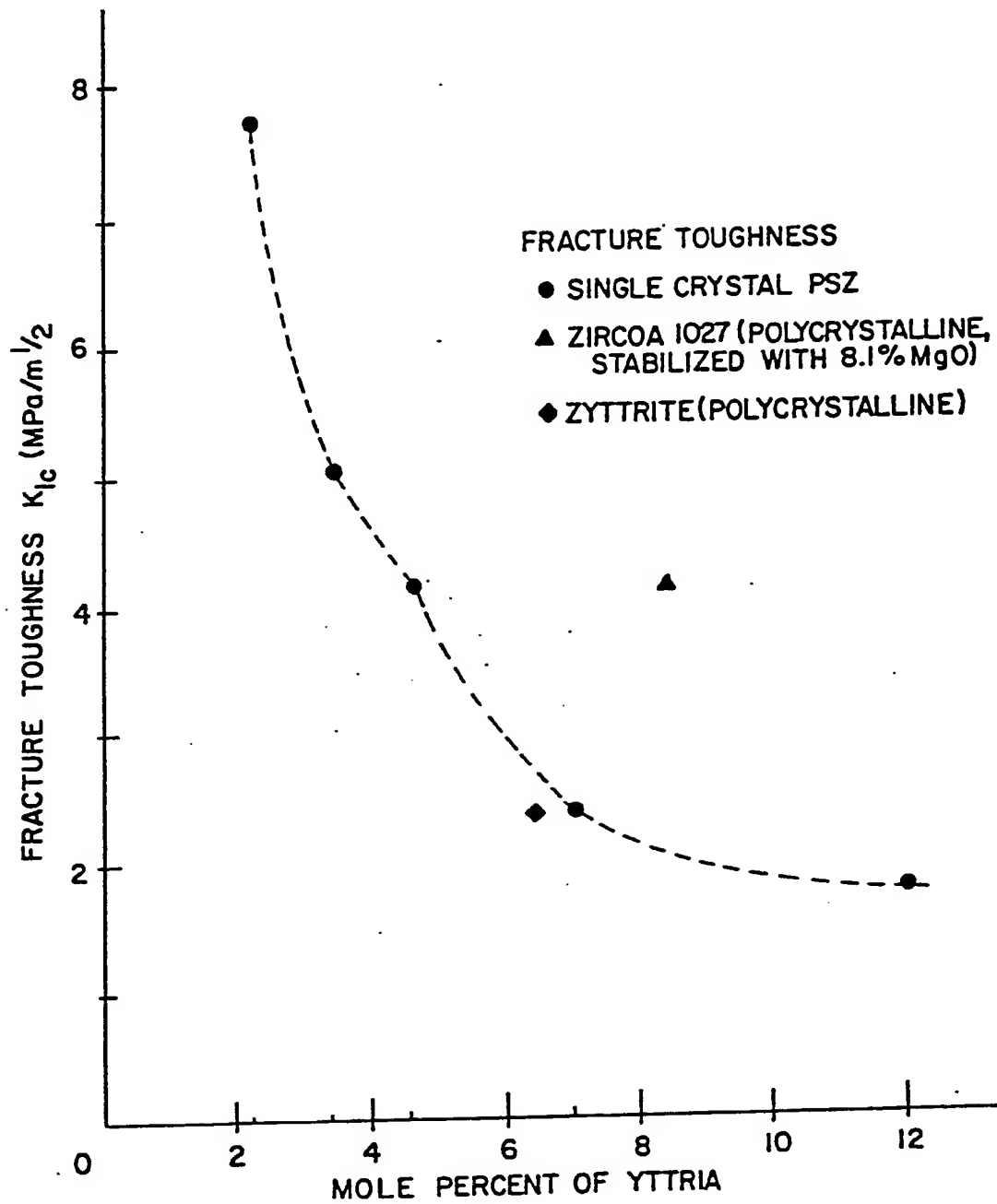
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*Fig.4*

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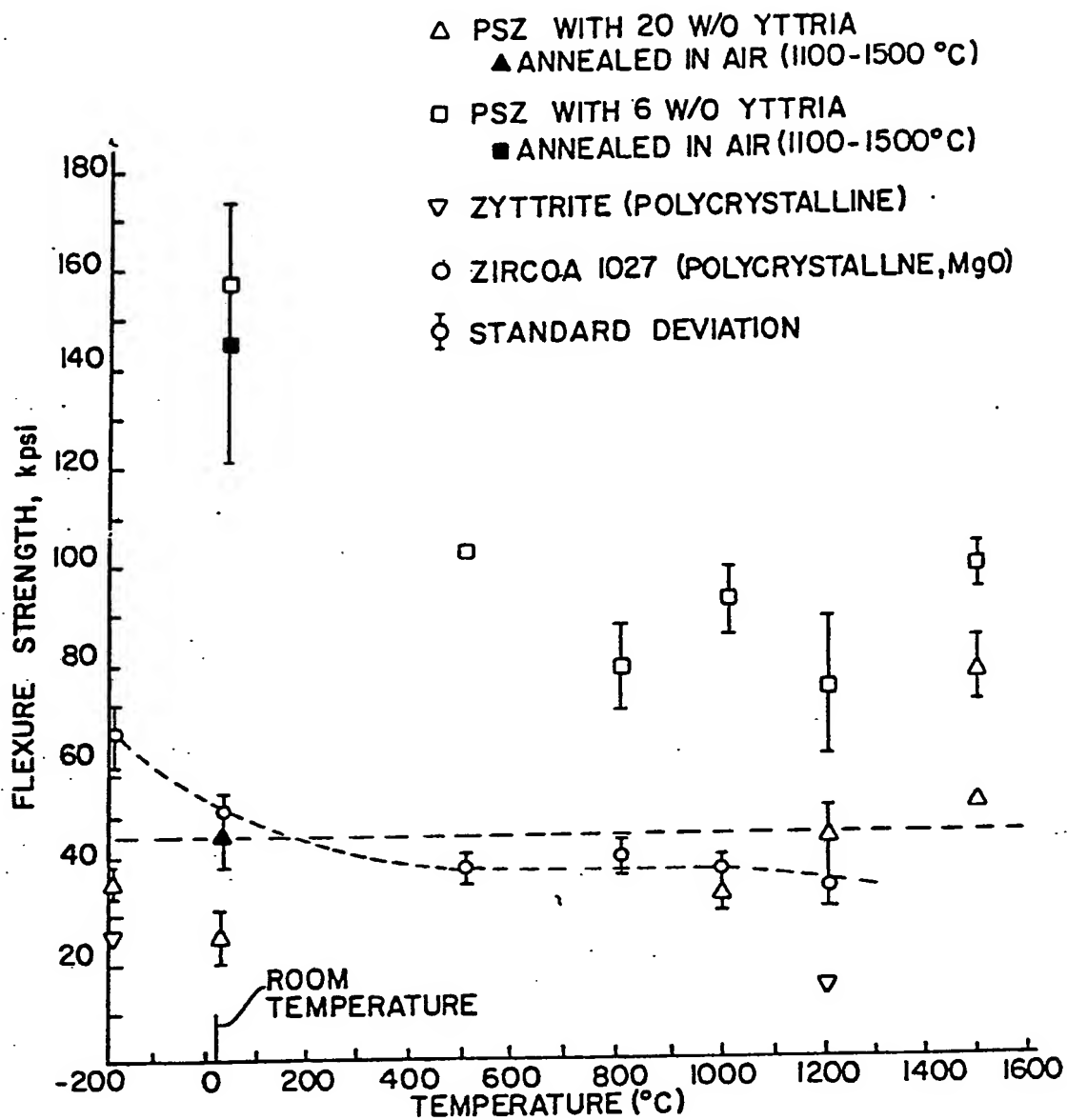
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*Fig.4A*

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*Fig.5*

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US82/00557

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. C30B 11/00		
U.S. CL. 156/616R		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	156/DIGEST 95; 106/42; 23/305RE, 293R	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US,A, 4,049,384, PUBLISHED 20 SEPTEMBER 1977, WENCKUS ET AL.	1-20
A	US,A, 4,153,469, PUBLISHED 08 MAY 1979, ALEXANDROV ET AL.	1-20
X	GB,A, 1,491,362, PUBLISHED 09 NOVEMBER 1977, ALEXANDROV ET AL.	1-20
A	GB,A, 1,373,888, PUBLISHED 13 NOVEMBER 1974, ALEXANDROV ET AL.	1-20
X	N, "MECHANISMS OF TOUGHENING PARTIALLY STABILIZED ZIRCONIA", JOURNAL OF THE AMERICAN CERAMIC SOCIETY, PUBLISHED MARCH 1977, VOLUME 60, PORTER ET AL.	1-20
A	N, "CUBIC ZIRCONIA", THE LAPIDARY JOURNAL, VOLUME 35, PAGES 1194-1200, 1210-1214, SEPTEMBER 1981, NASSAU.	1-20
<p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ²
01 JULY 1982		16 JUL 1982
International Searching Authority ¹		Signature of Authorized Officer ²⁵
ISA/US		GREGORY N. CLEMENTS